

# Lecture 6. Absorption by atmospheric gases in the IR, Visible and UV spectral regions.

## **Objectives:**

1. Absorption coefficient and transition function.
2. Gaseous absorption in IR.
3. Gaseous absorption in the visible and near infrared.
4. Gaseous absorption in UV.

## **Required reading:**

L02: 3.2, 4.2.1

## **Additional/advanced reading:**

Kyle T.G., Atmospheric transmission, emission and scattering. Pergamon Press, Oxford, 1991.

# 1. Absorption coefficient and transmission function.

**Absorption coefficient** is defined by the position, strength, and shape of a spectral line:

$$k_{\nu} = S f(\nu - \nu_0) \quad [7.1]$$

where  $S$  is the line intensity and  $f$  is the line profile:

$$S = \int k_{\nu} d\nu \quad \text{and} \quad \int f(\nu - \nu_0) d\nu = 1$$

**Table 7.1** Units used for path length (or amount of absorbing gases); absorption coefficient, and line intensity.

Absorbing gas (path length $u$ )	Absorption coefficient	Line intensity ( $S$ )
cm	$\text{cm}^{-1}$	$\text{cm}^{-2}$
$\text{g cm}^{-2}$	$\text{cm}^2 \text{g}^{-1}$	$\text{cm g}^{-1}$
$\text{cm}^{-2}$	$\text{cm}^2$	cm
cm atm	$(\text{cm atm})^{-1}$	$\text{cm}^{-2} \text{atm}^{-1}$

*Units of the line profile,  $f$ :* LENGTH (often cm)

***Dependencies:***

S depends on **T**;

$f(\nu - \nu_0, \alpha)$  depends on the line halfwidth  **$\alpha$  (p, T)**, which depends on pressure and temperature.

**Monochromatic transmission function** may be defined as

$$\boxed{T_v = \exp(-\tau_v)} \quad [7.2]$$

where

$\tau_v$  is the optical depth  $\tau = \int_u^{u_1} k_v du$

and  $u$  is the **path length** defined as  $u = \int_{z_1}^{z_2} \rho(z) dz$

**NOTE:** same name: Transmission function = Transmittance

**Homogeneous absorption path:**

when  $k_\nu$  does not vary along the path and thus  $\tau = k_\nu u$

**Inhomogeneous absorption path:**

when  $k_\nu$  varies along the path

**NOTE:** In general,  $\tau_\nu$  depends on both the wavenumber and path length.

## 2. Gaseous absorption in IR.

**Main atmospheric gases absorbing/emitting in IR: CO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CFCs.**

- Each atmospheric gas has a specific absorption/emission spectrum – its own signature.

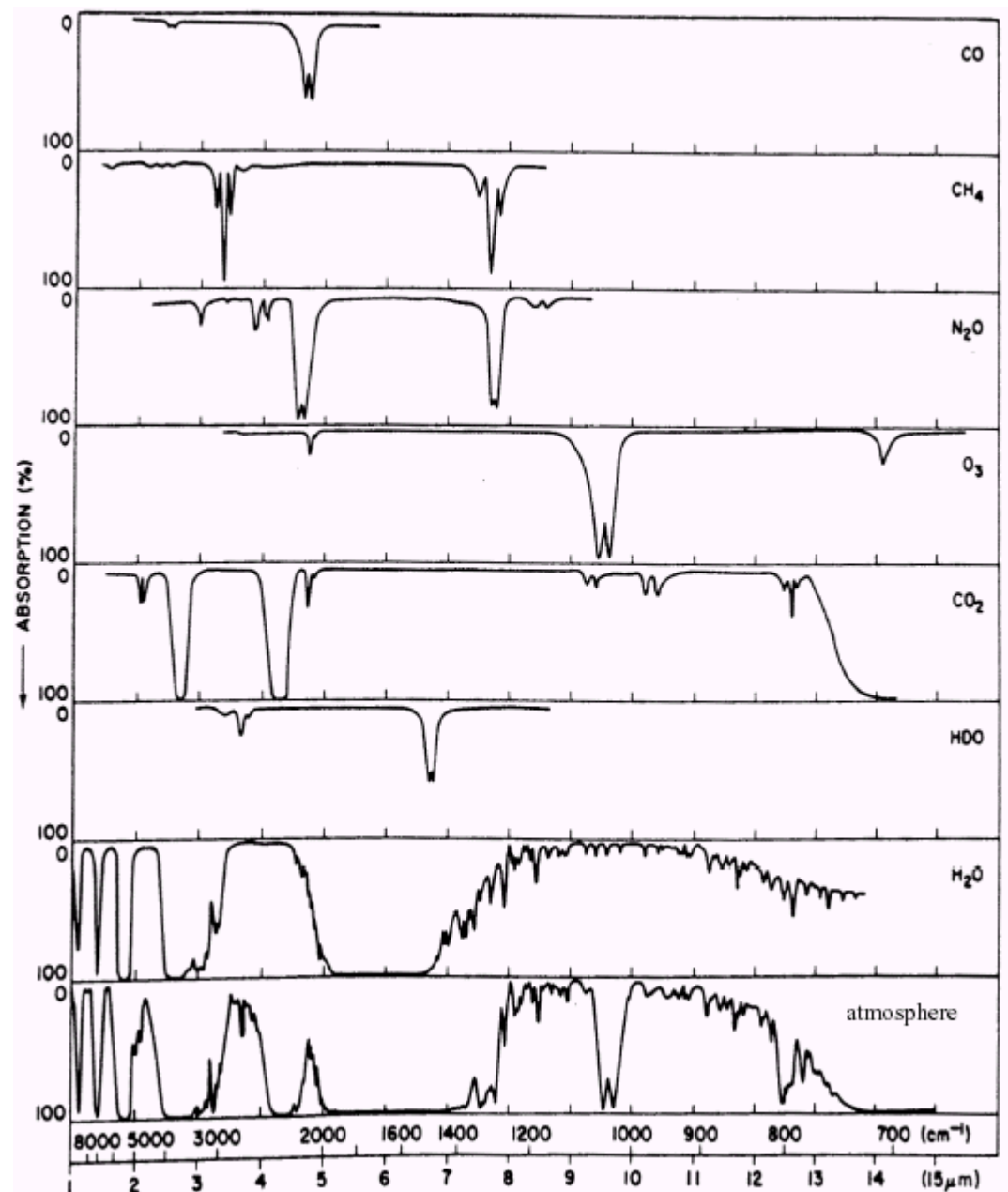
**Table 7.2** The most important vibrational and rotational transitions for H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and CFCs.

Gas	Center $\nu$ (cm <sup>-1</sup> ) ( $\lambda$ ( $\mu$ m))	Transition	Band interval (cm <sup>-1</sup> )
<b>H<sub>2</sub>O</b>	- 1594.8 (6.3) continuum*	pure rotational  $\nu_2$ ; P, R  far wings of the strong lines; water vapor dimers (H <sub>2</sub> O) <sub>2</sub>	0-1000  640-2800  200-1200

\* Continuum absorption by water vapor in the region from 800-1200 cm<sup>-1</sup> remains unexplained. It has been suggested that it results from the accumulated absorption of the distant wings of lines in the far infrared. This absorption is caused by collision broadening between H<sub>2</sub>O molecules (called **self-broadening**) and between H<sub>2</sub>O and non-absorbing molecules (N<sub>2</sub>) (called **foreign broadening**).

Gas	Center $\nu$ ( $\text{cm}^{-1}$ ) ( $\lambda(\mu\text{m})$ )	Transition	Band interval ( $\text{cm}^{-1}$ )
<b>CO<sub>2</sub></b>	667 (15) 961 (10.4) 1063.8 (9.4) 2349 (4.3)	<div> <div>v<sub>2</sub>; P, R, Q</div> <div> <div>]</div> <div>overtone and combination</div> </div> <div>v<sub>3</sub>; P, R</div> <div>overtone and combination</div> </div>	540-800 850-1250  2100-2400
<b>O<sub>3</sub></b>	1110 (9.01) 1043 (9.59) 705 (14.2)	v <sub>1</sub> ; P, R v <sub>3</sub> ; P, R v <sub>2</sub> ; P, R	950-1200 600-800 600-800
<b>CH<sub>4</sub></b>	1306.2 (7.6)	v <sub>4</sub>	950-1650
<b>N<sub>2</sub>O</b>	1285.6 (7.9) 588.8 (17.0) 2223.5 (4.5)	v <sub>1</sub> v <sub>2</sub> v <sub>3</sub>	1200-1350 520-660 2120-2270
<b>CFCs</b>			700-1300

**Figure 7.1** Low-resolution infrared absorption spectra of the major atmospheric gases.



### 3. Gaseous absorption then in the Visible and near-IR

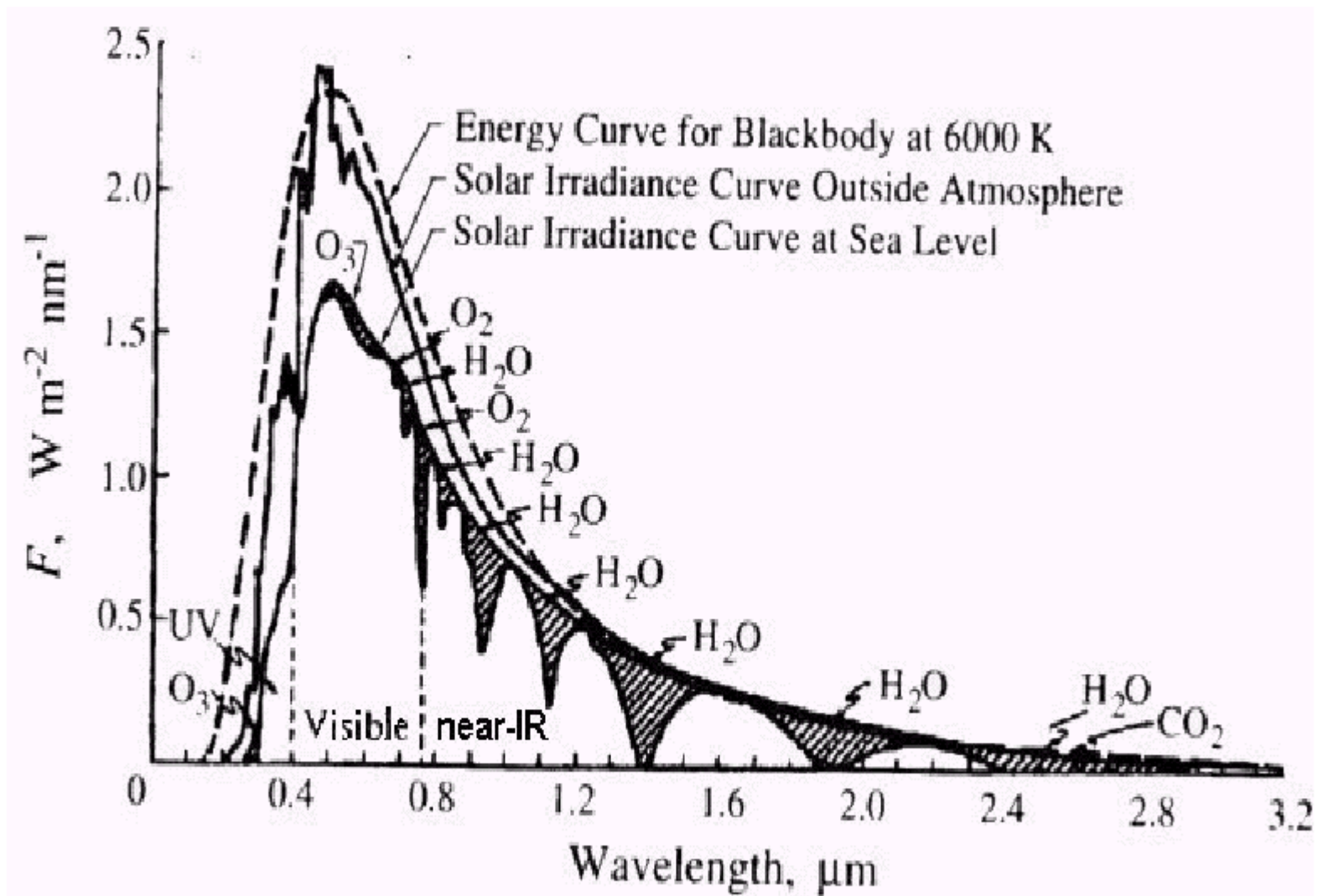
- Absorption of visible and near IR radiation in the gaseous atmosphere is primarily due to H<sub>2</sub>O, O<sub>3</sub>, and CO<sub>2</sub>.

**Table 7.3** Main Visible and near-IR absorption bands of atmospheric gases

Gas	Center $\nu$ (cm <sup>-1</sup> ) ( $\lambda$ ( $\mu$ m))	Band interval (cm <sup>-1</sup> )
H <sub>2</sub> O	3703 (2.7)	2500-4500
	5348 (1.87)	4800-6200
	7246 (1.38)	6400-7600
	9090 (1.1)	8200-9400
	10638 (0.94)	10100-11300
	12195 (0.82)	11700-12700
	13888 (0.72)	13400-14600
	visible	15000-22600
CO <sub>2</sub>	2526 (4.3)	2000-2400
	3703 (2.7)	3400-3850
	5000 (2.0)	4700-5200
	6250 (1.6)	6100-6450
	7143 (1.4)	6850-7000



Gas	Center $\nu$ (cm <sup>-1</sup> ) ( $\lambda$ ( $\mu$ m))	Band interval (cm <sup>-1</sup> )
<b>O<sub>3</sub></b>	2110 (4.74) 3030 (3.3) visible	2000-2300 3000-3100 10600-22600
<b>O<sub>2</sub></b>	6329 (1.58) 7874 (1.27) 9433 (1.06) 13158 (0.76) 14493 (0.69) 15873 (0.63)	6300-6350 7700-8050 9350-9400 12850-13200 14300-14600 14750-15900
<b>N<sub>2</sub>O</b>	2222 (4.5) 2463 (4.06) 3484 (2.87)	2100-2300 2100-2800 3300-3500
<b>CH<sub>4</sub></b>	3030 (3.3) 4420 (2.20) 6005 (1.66)	2500-3200 4000-4600 5850-6100
<b>CO</b>	2141 (4.67) 4273 (2.34)	2000-2300 4150-4350
<b>NO<sub>2</sub></b>	visible	14400-50000



**Figure 7.2** Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

**NOTE:** Atmospheric gases absorb only a small fraction of visible radiation.

## 4. Gaseous absorption in UV.

**NOTE:** Various forms of internal energy of a molecule were defined and discussed in Lecture 6. Recall that  $E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}}$

**Electronic energy  $E_{\text{el}}$**  originates in the unstable configurations of electrons in atoms and molecules.

- **Electrons on inner orbits** (close to the atomic nucleus) can be disturbed or dislodged only by photons having the large energies (short-wave UV and X-rays);
- **Electrons on the outermost orbits** can be disturbed by the photons having the energies of UV and visible radiation => these electrons are involved in absorption/emission in the UV and visible.
- Both an atom and a molecule can have the **electronic transitions**. Electronic transitions of a molecule are always accompanied by vibrational and rotational transitions and are governed by numerous selection rules.

- To avoid very complicated calculations of electronic transitions, numerous measurements of the **absorption cross-sections** of the atmospheric atoms and molecules absorbing in the UV and visible have been performed in laboratory experiments.
  - In general, the absorption cross section varies with temperature.

**NOTE:** Absorption cross-sections can be determined in the laboratory using the Beer-Bouguer-Lambert law (recall Lecture 2). In such an experiment, from a measure of the light intensity in the absence of sample ( $I_0$ ) and in the presence of a sample ( $I$ ) through a vessel of length  $l$  containing a known concentration ( $N$ ) of absorbing gas, one can obtain the absorption cross-sections from

$$\frac{I_{\lambda}}{I_{0,\lambda}} = \exp(-\sigma_{a,\lambda} Nl)$$

**NOTE:** Recall Lecture 2: for a known absorption cross-section  $\sigma_{a,\lambda}$ , the absorption coefficient is calculated as  $\beta_{a,\lambda} = \sigma_{a,\lambda} N$

where  $N$  is the number of molecules of a given gas per unit volume of air.

- Electronic transitions (i.e. high-energy UV photons) may cause various photochemical and photophysical processes.

Absorption of a high-energy photon ( $AB + h\nu \rightarrow AB^*$ ) may result in the following primary **photophysical** and **photochemical** processes:

**Luminescence:**  $AB^* \rightarrow AB + h\nu_l$

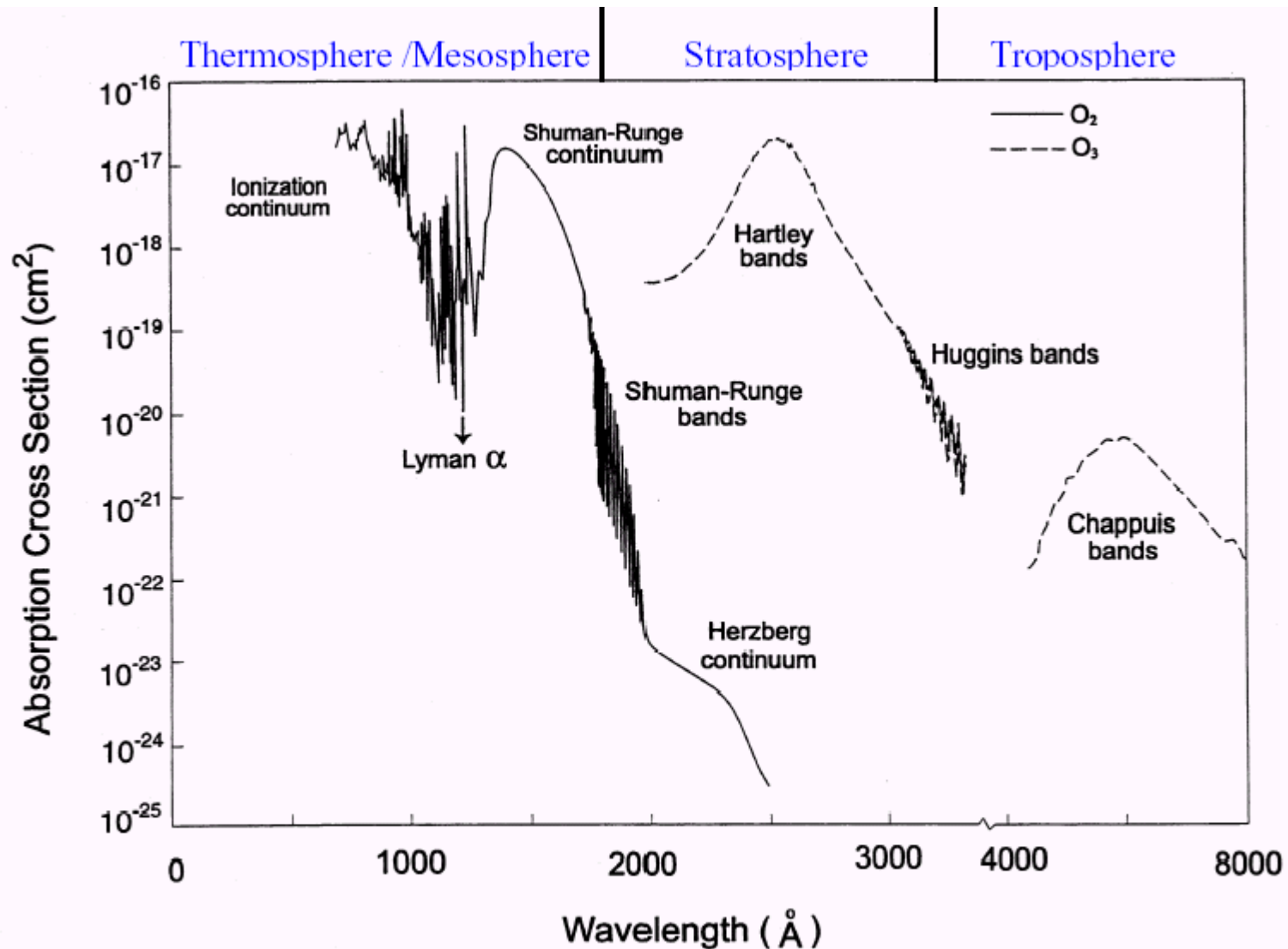
**Ionization:**  $AB^* \rightarrow AB^+ + e$

**Quenching:**  $AB^* + M \rightarrow AB$  (M represent any molecule that can carry away energy)

**Dissociation:**  $AB^* \rightarrow A + B$

**Chemical reaction:**  $AB^* + C \rightarrow A + BC$

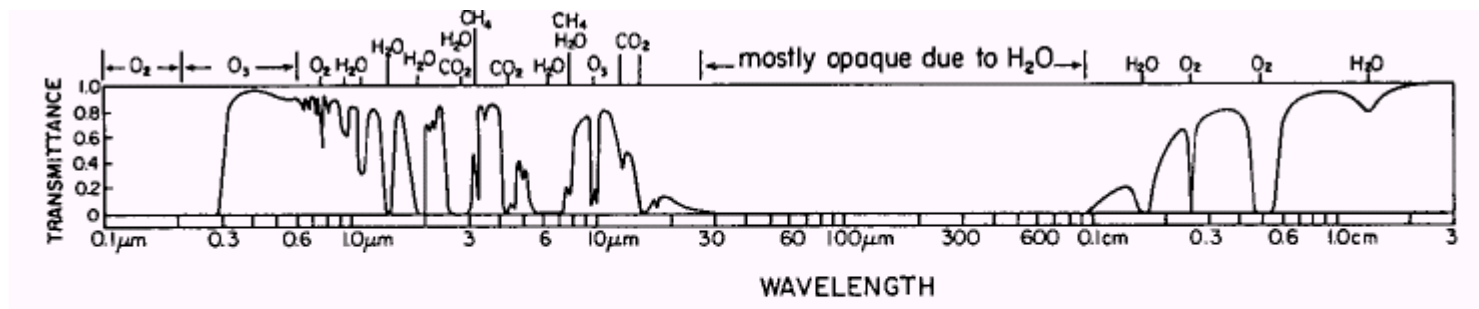
- Absorption of UV radiation in the gaseous atmosphere is primarily due molecular oxygen  $O_2$  and ozone  $O_3$ .



**Figure 7.3** Spectral absorption cross-sections of  $O_2$  and  $O_3$

## NOTE:

- a) Bands of  $O_2$  and  $O_3$  at wavelengths  $< 1 \mu m$  are electronic transitions.
- b) These absorption bands are relatively uncomplicated continua because practically all absorption results in dissociation of the molecule (so the upper state is not quantized);
- c) Despite the small amount of  $O_3$ , no solar radiation penetrates to the lower atmosphere at wavelengths  $< 310 \text{ nm}$  (because of large absorption cross-sections of  $O_3$ );



Low resolution transmission modeled spectrum of the Earth's atmosphere showing molecular absorption bands at all wavelengths. [Kidder and Vonderhaar, Fig. 3.14]

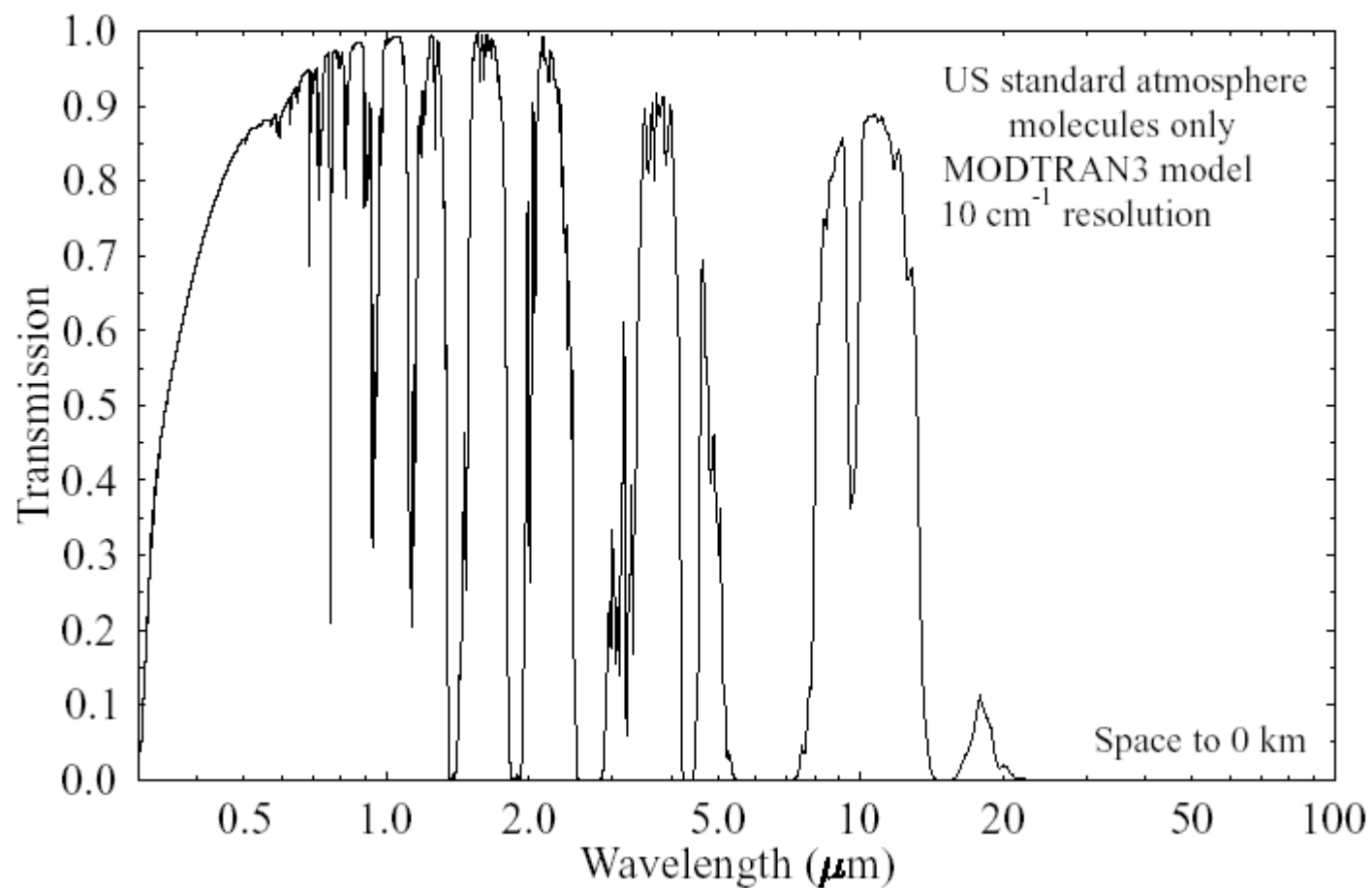
**Table 7.3** Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

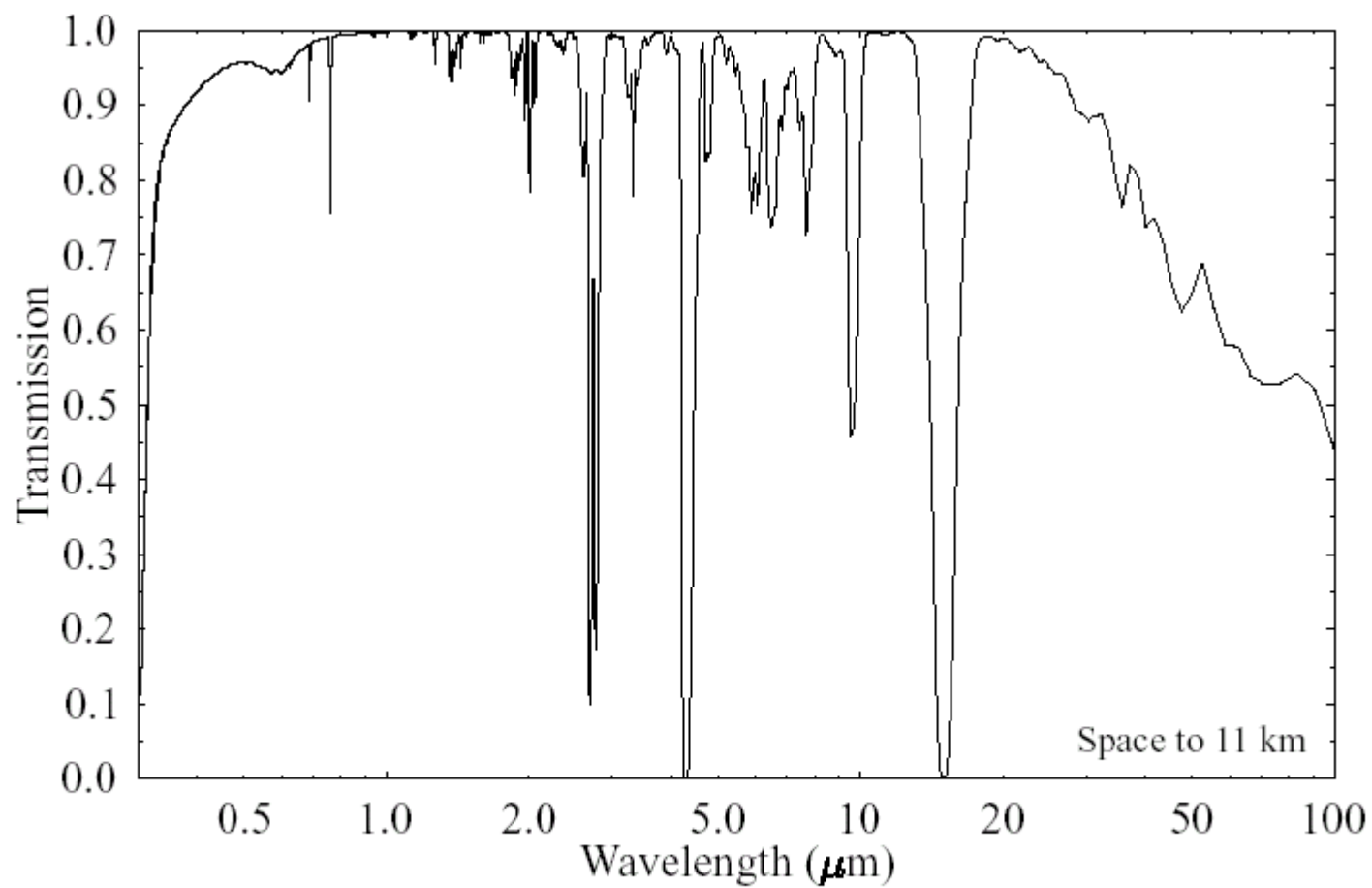
Gas	Absorption wavelengths ( $\mu\text{m}$ )
$\text{N}_2$	< 0.1
$\text{O}_2$	< 0.245
$\text{O}_3$	0.17-0.35
	0.45-0.75
$\text{H}_2\text{O}$	< 0.21
	0.6-0.72
$\text{H}_2\text{O}_2$ hydrogen peroxide	< 0.35
$\text{NO}_2$ nitrogen oxide	< 0.6*
$\text{N}_2\text{O}$	< 0.24
$\text{NO}_3$ nitrate radical	0.41-0.67
$\text{HONO}$ nitrous acid	< 0.4
$\text{HNO}_3$ nitric acid	< 0.33
$\text{CH}_3\text{Br}$ methyl bromide	< 0.26
$\text{CFCl}_3$ (CFC11)	< 0.23
$\text{HCHO}$ formaldehyde	0.25-0.36

\*  $\text{NO}_2$  absorb at  $\lambda < 0.6 \mu\text{m}$ , but photodissociate at  $\lambda < 0.4 \mu\text{m}$



## Earth Transmission Spectra





Low resolution transmission spectrum of the atmosphere down to the surface and to the tropopause.

# HITRAN spectral database

The 2000 HITRAN Database contains over 1,000,000 spectral lines for 36 different molecules. Information and database is at <http://www.HITRAN.com/>.  
The 1996 HITRAN Database is available on CD-ROM.

Relevant quantities in HITRAN database:

- $\nu_0$  Transition frequency ( $\text{cm}^{-1}$ )
- $S$  Strength at  $T_0 = 296$  K (cm/molecule)
- $\alpha_{L,air}^0$  air broadened halfwidth ( $\text{cm}^{-1}/\text{atm}$ ) at 296 K
- $\alpha_{L,self}^0$  self broadened halfwidth ( $\text{cm}^{-1}/\text{atm}$ ) at 296 K
- $E_L$  Lower state energy ( $\text{cm}^{-1}$ )
- $n$  temperature dependence coefficient for halfwidth

Table 6. Example of direct image of line parameters.

Mol/ Iso	$\nu_0$	S	$ R ^2$	$\gamma_{air}$	$\gamma_{self}$	$E''$	n	$\delta$	$\nu'$	$\nu''$	$Q'$	$Q''$	IER	IREF
21	800.450992	3.198E-26	6.578E-05	0.0676	0.0818	2481.5624	.78	.000000	14	6		P 37	465	1 1 1
291	800.454690	3.242E-22	0.000E+00	0.0845	0.1750	369.6303	.94	.000000	9	1341519	331419		000	4 4 1
291	800.454690	9.724E-22	0.000E+00	0.0845	0.1750	369.6303	.94	.000000	9	1341619	331519		000	4 4 1
121	800.455380	1.037E-22	1.596E-03	0.1100	0.0000	530.3300	.75	.000000	32	1446 740	45 640		000	4 4 1
121	800.455380	1.037E-22	1.596E-03	0.1100	0.0000	530.3300	.75	.000000	32	1446 640	45 540		000	4 4 1
101	800.456932	5.190E-23	5.133E-04	0.0670	0.0000	851.0515	.50	.000000	2	145 244	-44 143	-301	3 3 1	
121	800.457760	4.726E-23	4.446E-03	0.1100	0.0000	920.0900	.75	.000000	32	14502822	492722		000	4 4 1
121	800.457760	4.726E-23	4.446E-03	0.1100	0.0000	920.0900	.75	.000000	32	14502922	492822		000	4 4 1
24	800.465942	9.794E-27	6.064E-04	0.0754	0.1043	1341.2052	.69	.000000	8	3		R 13	425	1 1 1

FORMAT (I2,I1,F12.6,1P2E10.3,0P2F5.4,F10.4,F4.2,F8.6,2I3,2A9,3I1,3I2) corresponding to:

Mol	I2-	Molecule number
Iso	I1-	Isotope number (1= most abundant, 2= second most abundant, etc.)
$\nu_o$	F12.6-	Frequency in $\text{cm}^{-1}$
S	E10.3-	Intensity in $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$ @ 296K
$ R ^2$	E10.3-	Transition probability-squared in Debye <sup>2</sup>
$\gamma_{\text{air}}$	F5.4-	Air-broadened halfwidth (HWHM) in $\text{cm}^{-1}/\text{atm}$ @ 296K
$\gamma_{\text{self}}$	F5.4-	Self-broadened halfwidth (HWHM) in $\text{cm}^{-1}/\text{atm}$ @ 296K
$E''$	F10.4-	Lower state energy in $\text{cm}^{-1}$
n	F4.2-	Coefficient of temperature dependence of air-broadened halfwidth
$\delta$	F8.6-	Air-broadened pressure shift of line transition in $\text{cm}^{-1}/\text{atm}$ @ 296K
$\nu', \nu''$	2I3-	Upper state global quanta index, lower state global quanta index
$Q', Q''$	2A9-	Upper state local quanta, lower state local quanta
IER	3I1-	Accuracy indices for frequency, intensity, and air-broadened halfwidth
IREF	3I2-	Indices for table of references corresponding to frequency, intensity, and halfwidth

The format of the HITRAN 1996 and 2000 database. The HITRAN 2001 format will be the same, except  $|R|^2$  is replaced by the Einstein A coefficient and the  $\nu', \nu'', Q', Q'', \text{IER}, \text{IREF}$  formats are expanded.

#### APPENDIX B. HITRAN Molecules with Associated Indices

HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines	HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines
1	H <sub>2</sub> O	49444	21	HOCl	15565
2	CO <sub>2</sub>	60802	22	N <sub>2</sub>	120
3	O <sub>3</sub>	275133	23	HCN	772
4	N <sub>2</sub> O	26174	24	CH <sub>3</sub> Cl	9355
5	CO	4477	25	H <sub>2</sub> O <sub>2</sub>	5444
6	CH <sub>4</sub>	48032	26	C <sub>2</sub> H <sub>2</sub>	1668
7	O <sub>2</sub>	6292	27	C <sub>2</sub> H <sub>6</sub>	4749

HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines	HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines
8	NO	15331	28	PH <sub>3</sub>	2886
9	SO <sub>2</sub>	38853	29	COF <sub>2</sub>	54866
10	NO <sub>2</sub>	100680	30	SF <sub>6</sub>	11520
11	NH <sub>3</sub>	11152	31	H <sub>2</sub> S	7151
12	HNO <sub>3</sub>	165426	32	HCOOH	3388
13	OH	8676	33	HO <sub>2</sub>	26963
14	HF	107	34	O	2
15	HCl	533	35	ClONO <sub>2</sub>	32199
16	HBr	576	36	NO <sup>+</sup>	1206
17	HI	237	37	HOBr	4358
18	ClO	7230			
19	OCS	858			
20	H <sub>2</sub> CO	2702			